A Molecular Optical Channel Model based on Phonon-Assisted Energy Transfer Phenomenon

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***Abstract*—Recent progress in the field of nanotechnology is enabling communication between nanodevices to be considered also for *in-vivo* applications. In particular, nanodevices enabling light-controlled process have started to attract a lot of interest in the research community, due to potential applications like healthcare wearable devices, intra-body applications and optogenetics, whose main objective is to stimulate neurons by the means of the light signals.**

Leveraging on these premises, we consider upconversion phenomenon, namely the ability of specific nanoparticles to convert low energy radiations (*e.g.*, near-infrared radiations) into higher energy radiation (*e.g.*, visible light) via a non-linear process. Energy transfer as viable communication mean has been already considered based on Förster-Resonance-Energy Transfer. In this paper, we focus on Phonon-Assisted Energy Transfer, and we analyze the requirements and conditions for generating optical signals from a genuine signal processing point of view. More specifically, based on information theory approach, we derive the conditions to minimize the error probability. We show that the dopant concentration (*i.e.*, concentration of elements drugging a pure material in order to change its features) mostly influences the correct generation of the light signal. The performed analysis is based on experimental results taken from [1], [2].

***Index Terms*—Upconversion process, optical channel, rare-earth doped fluorophores, Bit Error Ratio.**

I. Introduction

Recently, nanocommunication paradigm has appeared as a very intriguing research domain [3] and different communication approaches have been proposed ranging from chemical, molecular to acoustic solutions. Based on the specific application domain, a communication paradigm can present more pertinent features than others. However, one of the main and most important application domain of nanocommunications is biomedical applications, and more specifically *in-vivo* applications such as drug delivery, diagnostics, and therapy.

Biological and *in-vivo* applications are characterized by specific requirements and constraints that have to be explicitly considered and integrated in the communication paradigm, such as the low toxicity level of the devices involved, as well as the type of power source and signal adopted, and biodegradability of the components. From a communication and information theory point of view, it is highly desirable to have a high signal-to-noise ratio, a reduction of noise, and acceptable transmission delay.

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One of the most promising candidates for nanocommunications in biomedicine is *molecular communication paradigm* [4], [5], which is an active research area. Many different approaches have been considered such as encoding the information on the concentration, the type, and the release time of molecules that are propagating in the environment with the help of diffusion [3]. However, in this diffusion-based approach, the dynamics of the system is really slow causing high latency and very low transmission rate.

By keeping in mind the main requirements in terms of biodegradability, low biotoxocity level, and effectiveness from an information theory point of view, we investigate a different approach based on the *upconversion phenomenon* to mitigate the latency problem. This mechanism consists of the conversion capability from near infrared radiations (NIR) with a lower energy level into visible radiations with a higher energy level. This phenomenon can be the mean for enabling molecular communication through optical signals. Indeed, the acquisition of optical signal generation control provides a huge capability to transfer information in a biological context.

In this paper, we focus on upconversion (UC) photoluminescence as represented in Fig. 1. Two nanoparticles (NPs) acting as donor/transmitter and acceptor/receiver, respectively, exchange energy at a given distance R (see Fig. 1(a)). The activation of the communication can be either caused by an external source (*e.g.*, a NIR laser [6]) or a phosphorescence due to the binding of a neighbor cell with a toxin. It is worth to notice that the communication system considered in this paper is constituted by nanoparticles communicating with each other. The communication is inside the same node (*intra-cell communication*) by the means of Phonon-Assisted Energy Transfer, and among nanoparticles belonging to different cells/nodes (*inter-cell communication*) by the means of optical signals, as depicted in Fig. 1(a) and Fig. 1(b), respectively. The distance d represents the distance achievable by the luminous signal and depends on the specific environment considered (*e.g.*, human tissue, blood cells, etc.) and on the wavelength of the emitted signal. In general, it can be considered on the order of some few millimeters [7]. In this work, we will focus on the *intra-cell communication*, since we need a robust generation of optical signals to make the *inter-cell communication* feasible.

The UC phenomenon is also called *anti-Stokes photoluminescence* since it violates the Stokes' law stating that the wavelength of the emitted light by photoluminescence is longer than the wavelength of the exciting light. It is based on an additional energy gain that allows the fill-up of the gap existing between a "donor" and an "acceptor", induced by multiple

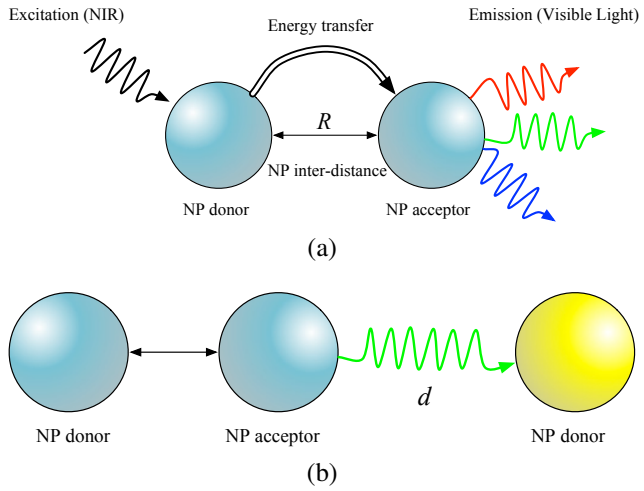

Fig. 1. Schematic representation of the upconversion phenomenon based on an incident infrared radiation with a visible light radiation emission. In the case of nanomedicine applications, the nanoparticles are inside the human body. (a) In the specific context a couple of donor/acceptor nanoparticles (*light-blue NPs*) are positioned in the same cell. This means that within a single node there is an energy/information transfert (*intra-cell communication*). (b) The NP acceptor will emit an optic signal (*e.g.*, in the visible light spectrum) reaching an external NP donor (*yellow NP*) at distance d (*inter-cell communication*).

photons or thermal phonon energy absorption [8]. Phonons are designated as quasi-particles derived from vibrations of atoms in solids. In this work we focus on these particles as enabler of energy transfer, and then information transfer. Communication schemes based on phonons as main information carriers have been already investigated in a different context in [9], [10].

The UC phenomenon occurs in specific materials such as RE(rare-earth)-doped materials and some organic dyes, thanks to their particular electronic structure. Moreover, RE-doped upconversion nanoparticles show this ability to convert long wavelength NIR into short wavelength visible radiation via a non-linear process. Indeed, traditional processes are linear and the emitted wavelength is higher than the excitation source wavelength. This means that the associated energy to the emitted signal is lower than that associated to the input. Since UC typically involves at least two or more photons/phonons, as consequence the process is non-linear [6].

It has been highlighted that this kind of nanoparticles can overcome some limitations of fluorescent probes, quantum dots, and organic dyes [11]. For example, upconversion nanoparticles (UNPs) have a higher signal-to-noise ratio (SNR) as compared to quantum dots and organic dyes, due to a reduction of autofluorescence in UNPs, a higher sensitivity detection and the NIR light source is less absorbed by the tissue allowing a deeper penetration into tissue.

As shown in Fig. 1, a typical application scenario consists of several functionalized cells, where nanoparticles are integrated and make a single cell as an optical source able of emitting different types of optical signals ranging from NIR to visible light and ultra-violet range [12], [13]. In this paper, we aim to analyze the specific conditions influencing the optical signal generation and we will perform this analysis through an information theory approach.

Motivated by the above considerations, in this paper:

- We analyze RE-doped nanomaterials and their associated features, which could pave the way towards the modeling of a new and revolutionary molecular communication paradigm that exploits the UC mechanism and generates optical signals;
- We investigate the UC phenomenon, by exploiting the Phonon-Assisted non-radiative Energy Transfer (PAET) mechanism, and capture the main features of different RE-doped nanomaterials that could be of interest as enabler for a molecular communication paradigm;
- We model a basic PAET-based UC communication channel;
- We perform an information theory analysis of UC-based system using experimental results taken from [1], [2], and then we give a perspective on the results obtained in terms of channel capacity.

The rest of the paper is organized as follows. In Section II, we revise the main contributions in literature regarding UC phenomenon and rare-earth-doped materials. In Section II, we then propose our UC-based communication channel, while in Section IV, we perform an information theory based analysis of the channel. The assessment of the proposed model has been carried out through simulation results based on real experimental data taken from the literature. Finally, Section VI concludes the paper and also highlights potential directions.

II. Related Work and Motivation

Recently, the fervent research activity related to upconversion topic has allowed a precise control in terms of emission color, lifetime and intensity that make UC a good candidate for different practical applications. As shown in several literature contributions, UC phenomenon –and specifically, upconversion nanoparticles– have been considered mainly for biomedical applications. In particular, this phenomenon can be effectively exploited for drug delivery, bio-detection, fluorescence imaging, etc. [14]–[19].

UC phenomenon is based on inorganic crystalline embedded in a host lattice. In order to have an efficient UC process, the physically intermediate states between the ground state and the emitting state have to behave as energy reservoirs. An example of this type of crystalline elements are specific types of fluorophores, a.k.a RE-doped Apatite nanoparticles (REANPs). In particular, bioapatite has been shown to be very promising for biomedical applications because of its low toxicity level and high biocompatibility and biodegradability [20]. Apatite group is diffusely used as mineral and recently there have been several biomaterials based on apatite. Of course, the down-sizing of apatite host results in modification of its properties compared to microsized hosts because of quantum confinement effect. In [21], the authors show that Apatite nanoparticles (ANPs) have a high affinity level to biopolymers and low toxicity. Thanks to these specific features, bioapatite has been extensively used for hard tissue repair, drug delivery [22].

There are different types of upconversion luminescence mechanisms. Three basic approaches are recognized *i.e.*, (*i*) Excited State Absorption (ESA), (*ii*) Photon Avalanche (PA),

and (*iii*) Energy Transfer Upconversion (ETU). In this work we focus on ETU since it is recognized as the most efficient upconversion mechanism with doped nanomaterials based on Rare-Earth. It is also more interesting, since it is independent of pump power. In ETU, three types of energy transfer may occur such as (*i*) Resonant Radiative Energy Transfer (RRET), (*ii*) Resonant non-radiative Energy Transfer (RET), and (*iii*) Phonon-Assisted non-radiative Energy Transfer (PAET). The first mechanism (*i.e.*, RRET) occurs between an activator and a sensitizer –a.k.a. donor and acceptor, respectively–, and involves a photon emitted by a donor and absorbed by an acceptor. Depending on the degree of spectra overlapping of the donor-acceptor pair, the shape of the donor emission changes according to the acceptor concentration. The energy transfer probability (*i.e.*, P_{DA}) depends on the distance (*i.e.*, R) between the pair donor-acceptor as [6]:

$$P_{DA}(R) = \frac{\sigma}{4\pi R^2 \tau_d} \int g_d(\nu) g_a(\nu) d\nu, \tag{1}$$

where σ is the absorption cross-section, τ_d is the donor lifetime, and ν is the emitting frequency. In Eq. (1), the integral represents the donor-acceptor spectral overlap, namely g_d is the emission spectrum of the donor and g_a is the absorption spectrum of the acceptor.

The distance R depends on several factors and can be expressed as follows:

$$R \approx 2\left(\frac{3V}{4\pi C_{(A+D)} N}\right)^{1/3}, \tag{2}$$

where $C_{(A+D)}$ is the total concentration of dopant (acceptor plus donor), N is the number of available sites that the lanthanide ion can occupy in the unit cell, and V is the volume of the unit cell. It is worth to outline that the dopant ions are used to "drug" a material in order to change its features. In the specific context, dopants are of two types, *i.e.* (*i*) donor dopants and (*ii*) acceptor dopants.

In the case of RET, the energy transfer probability is given by:

$$P_{DA}(R) = \frac{R_0^n}{R^n \tau_d}, \tag{3}$$

where R_0 represents a critical transfer distance for which the excitation transfer and the spontaneous deactivation of the donor have the same probability. The exponent n is an integer that goes as $n = 6$ for dipole-dipole interaction, $n = 8$ for dipole-quadrupole interactions, and $n = 10$ for quadrupole-quadrupole interactions. Notice that the anti-Stokes emission efficiency of ETU is strongly dependent on the distance between ions, which is determined by the concentrations of ion dopants.

In the case of PAET, the pair donor-acceptor is characterized through Eq. (1) with different energy separations. In this case, the energy transfer probability goes to zero as the energy integral overlap in Eq. (1) goes to zero. However, it has been found that Rare-Earth (RE) ions energy differences of higher magnitude are possible and in this case multi-phonon processes must be considered [6], [23]. In practice, phonons work to fill in the energy gap.

Specifically, the second type of resonant energy transfer *i.e.*, RET, a.k.a. Förster-Resonance-Energy Transfer or Fluorescence Resonance Energy Transfer (FRET), has already been investigated as a phenomenon enabling communications among multiple molecules [24]. A MIMO approach based on FRET has been proposed in [25]. The same authors have proposed five different routing schemes based on FRET in [26], and they analyzed some open issues related to the specific features of FRET. We believe that some of these issues could be overcome by a PAET-based approach. In particular, FRET is high-distance sensitive, and little variations of distances could make the phenomenon not occurring. With recent technological advancements, the control of phonons has been enhanced and a PAET-based communication system could be more resilient.

In the context of biological applications such as nanomedicine, the nanodimension allows dodging the capture of macrophages, thus prolonged circulation in blood flow, and accumulation at the tumor site by "passive targeting" through the enhanced permeability and retention effect as nanocarrier [27]. Moreover, bioapatite shows high stability in normal cellular pH environment, but it is degradable at acidic environment, especially in tumor region, which allows drug release. The works in [28], [29] focus on the implementation of upconversion-based sensors. Specifically, Xu *et al.* [28] exploit the FRET process in order to detect specific ions, while Mattsson *et al.* [29] focus on the demonstration of how upconverting nanoparticles in FRET quantum dot systems can be used as effective tools for clinical diagnostics.

Another important feature of nanosized bioapatite is its structural capacity to accept many substitutions such as lanthanide ions as luminescent centers for offering an environment to sensitize the fluorescence of the dopant ions. Specifically, a dopant ion is a specific molecule that can be added in a host material in order to change specific properties of the matter.

For instance, fluorescent labeling has been shown as a fundamental tool in the study of complex biological interactions. Classical fluorescence cell labeling procedures were realized through the mean of fluorescent proteins, organic dyes, quantum dots, which present a series of disadvantages such as potential toxicity to the cells, simultaneous detection of multiple signals, and broad spectrum profile [20].

Generally speaking, RE-based UC nanomaterials have gained enormous attention, as a result of their advantages, such as low biotoxicity in tissues and deep penetration under near-infrared radiation and low photobleaching [22]. Photobleaching is an alteration of a molecule that makes it not enable to fluorescence. In a molecular communication scenario, a molecule showing photobleaching phenomenon cannot be used as transmitter. For that, low photobleaching is a desirable feature. UC-based nanoprobes cannot only enhance the detection sensitivity and signal-to-noise ratio, but also improve the penetration depth in tissue under the excitation of NIR light source. In [22], the authors use UNPs with pure red emission for *in-vivo* applications as bioimaging agents, illustrating the effectiveness of UNPs for a deeper penetration depth. Specifically, the authors present how the variation of

the concentration of some particular components makes it possible to vary the emission band of the nanoparticles from green/yellow to a near single red emission band. This result shows the potential of tuning optical components and gives some interesting insights to the study of rare-earth elements as dopant at different concentrations in a host material.

To the best of our knowledge, UNPs have never been considered as a viable way for modeling a molecular communication paradigm. Indeed, till now the recent intensive research activities on UNPs focus on biomedical and biological applications in the form of system imaging. However, the features of UNPs and the frequencies that they could be used as signal source, make them a very interesting technique for molecular communications. To summarize, the main purpose of our paper is to investigate on alternative communication paradigms as enabler of molecular communications. Bearing that in mind, we explore phenomena of energy transfer at ions and molecular level, since they represent a viable way to transmit information. However, the main difference between our work and FRET-based ones (*e.g.*, [30], [31]) is on the type of phenomenon that could overcome some of the inherent drawbacks of FRET. For instance, PAET does not require a strong spectral overlapping between donor and acceptor. This aspect could play a very important role if the technological advancements will allow a higher control on the generation of the phonons and above all on the energy associated to.

Finally, PAET-based systems are generally less sensitive to the distance, while FRET-based ones have been effectively used in clinical context and for molecular analysis thanks to the high distance sensitivity (see Eq. (1)). In general, in a communication context this could represent a strong constraint.

III. Upconversion Non-Resonant Optical Communication Channel

In this section, we present the UC phenomenon, accordingly adapted as a molecular communication technique based on optical signals. We then model the corresponding channel, where information is transferred from a transmitter node (*i.e.*, a donor molecule) to a receiver node (*i.e.*, an acceptor molecule).

In Fig. 2 we can observe the whole communication system as it will be considered in the next sections. An external source (*i.e.*, a NIR power laser) is applied to an NP donor. It is worth to notice that the communication process could also be activated by some internal chemical reactions, since there exist cells that binded with a specific toxin react by generating luminous signals.

It is worth to notice that an upconversion communication system is slightly different in respect of a traditional counterpart, since the transmitter and receiver are on the same structure/node. In practice we consider the *intra-cell communication* as trigger for an external *inter-cell communication*. We analyze *intra-cell communication* with an information theory approach in order to derive fundamental information for generating different optical signals. In this work, as in traditional systems, we associate a bit 0 to no-excitation and a bit 1 to the state of power laser excitation.

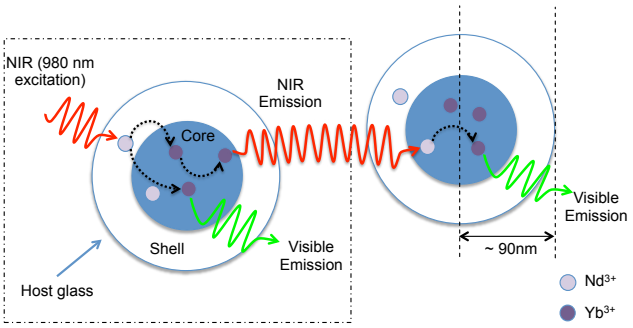

Fig. 2. Schematic of an host glass (*e.g.*, barium-alumino-metaphosphate) with donor (*i.e.*, Nd^{3+}) and acceptor (*i.e.*, Yb^{3+}) with variable concentration. Dotted area represents the system we are considering for data transmission. An external source (*e.g.*, a NIR laser) is applied to the system and a donor (*grey small circle*) is excited and generates an energy transfer towards an acceptor (*purple small circle*). Since multi-phonons are generated in correspondence to the acceptor, it will achieve a sufficient energy to emit a visible light output.

A very basic upconversion communication system is consisting of two ions identified respectively as *donor* and *acceptor*, corresponding to a transmitter and a receiver in a classical communication system, respectively. The donor is excited with a laser source and transmits energy to the acceptor. In On-Off Key (OOK) modulation system, the excitation corresponds to the need to transfer a bit 1 to the receiver, and then the energy transfer corresponds to an information transfer of a bit 1. The acquisition of an high control for tuning the wave emission is of paramount importance, since we could propagate the information transmission to other similar nanoparticles (as shown in Fig. 3), we could "illuminate" a specific area, conceive target-tracking solutions, etc. Based on these premises, we have realized that the type of information we are able to generate, highly depends on factors such as the concentration of donors and acceptor, the host material features, etc. and then we propose here to analyze the system from an information point of view.

In Fig. 3 we show an illustration of the mechanism that allows the visible light emission from the acceptor upon the excitation of donor with a NIR source. Firstly, an electron at its ground state (0) is excited with an infrared light beam that allows the electron to achieve the energy level (1) in donor (see phase (*a*) in Fig. 3). Then, in the phase (*b*) in Fig. 3 the electron of the acceptor achieves an energy level (2) through a non-radiative energy transfer from donor to acceptor based on a multi-phonons energy transfer (*i.e.*, PAET). When the excited electron at phase (2) relaxes to the ground-state (0), it emits visible light (see phase (*c*) in Fig. 3).

In order to better understand this phenomenon, let us consider the molecular system comprised of a couple of Neodymium and Ytterbium ions as acceptor and donor, respectively, *i.e.*, $Nd^{3+} \rightarrow Yb^{3+}$. The energy transfer process can be both resonant and non-resonant (*i.e.*, phonon-assisted) depending on the spectral overlapping between the donor band and the acceptor band. A large spectral overlapping is required for resonant energy transfer, while in the case there is no large spectral matching, the host phonon energy can fill in the energy

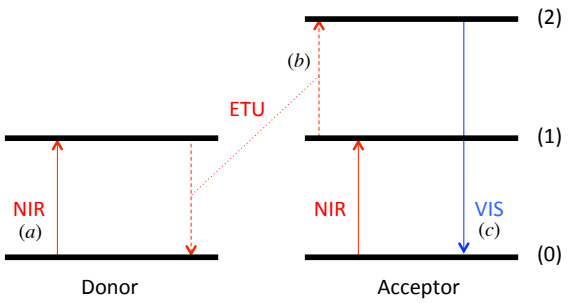

Fig. 3. Energy transfer upconversion mechanism, comprised of different phases. (*a*) An near infrared (NIR) light beam is used as excitation source for an electron at a ground state (0) in a donor ion, which is excited to the energy level (1). (*b*) Thanks to a non-radiative energy transfer (ETU), this electron achieves the energy level (2) in the acceptor ion. A multi-phonons energy transfer (PAET) mechanism occurs here. (*c*) When it reverts back to the ground state (0) still in the acceptor ion, it emits a visible light radiation (VIS).

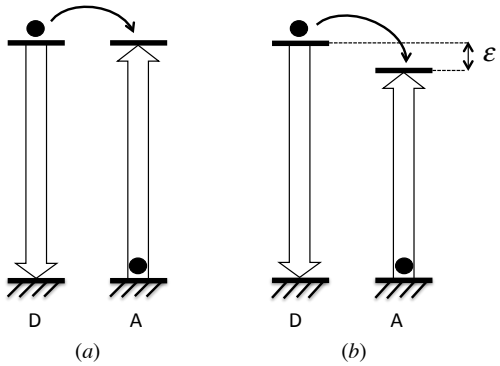

Fig. 4. Energy transfer process between a donor (D) and an activator (A) ion in the case of (*a*) resonant non-radiative transfer, and (*b*) phonon-assisted non radiative transfer.

gap between donor and acceptor. The couples $Nd^{3+} \rightarrow Yb^{3+}$ have been deeply investigated as rare-earth components in different host material showing both resonant and non-resonant behavior, so they represent an interesting case. In [32], the authors show an example of resonant process based on a ferroelectric laser crystal achieving 50% energy transfer efficiency. For the specific spectrum of Nd^{3+} and Yb^{3+} where there is a spectral mismatch between $Nd^{3+} - Yb^{3+}$ ions, in most of the systems, the energy transfer occurs as a *phonon-assisted process*. In this case, the host phonon energy plays a crucial role to fill the gap in terms of energy difference between the ions, as shown in Fig. 3. In the specific case of $Nd^{3+} \rightarrow Yb^{3+}$ systems, there is an energy difference of 1070 cm^{-1} [1], and then the host material which has a maximum phonon energy close to this value can achieve a high value of energy transfer efficiency.

A. FRET/PAET molecular communication systems

In [33] Kuscu and Akan considered a one-to-one communication scheme, with a *donor* and an *acceptor* node, based on FRET phenomenon. They assume that a donor is excited with a power laser and based on the specific conditions of reciprocal donor-acceptor distance on their emission-absorption spectra, which have to overlap, the FRET phenomenon can occur with a certain probability. In such a scenario, Kuscu and Akan [33] associate a bit 1 to the exciting power source at the beginning of a time slot, and a bit 0 otherwise. Based on this simple OOK modulation scheme, the authors derive a channel capacity analysis by varying different parameters, such as the reciprocal distance between donor and acceptor, and the orientation factor. In particular, the FRET process is a non-radiative energy transfer that can occur with specific fluorescent molecules such as polymers and organic dyes. As already outlined, in order the FRET process to occur, the overlapping area of the emission spectrum of the donor and the absorption spectrum of the acceptor must be large enough.

On the other hand, in the non-resonant UNPs case, this condition is not required, since the energy gap can be filled in through thermal low frequency phonons. In order to better clarify the difference between a resonant non-radiative transfer (*i.e.*, FRET) and a phonon-assisted non-radiative energy transfer (*i.e.*, PAET), we illustrated both in Fig. 4. We observe that for the resonant non-radiative energy transfer mechanism, an energy transfer between two ions at the same energy level is represented in Fig. 4 (*a*), while in the case of PAET there is a mismatch between the ions of donor and acceptor. This mismatch is represented by the energy gap ε in Fig. 4 (*b*).

Similar to the work in [33], in this paper we associate a bit 1 to the excitation with a pump power at the beginning of a time slot, and a bit 0 if there is no input at the beginning of a time slot. In the specific case we are considering, we are interested to investigate the impact of dopant concentration on the communication system performance. Optical and spectroscopic features of RE ions depend on host materials, and are strictly related with the concentration of RE ions on the host material. This suggests the possibility of tuning structural and optical properties of doped glasses, and then exploiting specific characteristics and properties as an improved Signal-to-Noise Ratio. This can have an important impact on the performance of a communication system based on phenomena such as PAET, which occurs in this type of glasses. For this reason, we do not isolate a sole donor and a sole acceptor as in [33]. Also, for the moment, we neglect external noise source such as self-quenching and multi-phonon relaxation. We assume a laser input is able to excite a donor, that has to propagate the information to an acceptor ion. In our case, we are considering Nd^{3+} ion as donor and Yb^{3+} ion as acceptor.

In the chosen donor-acceptor pair, we exploit the PAET model, since the ions involved have spectra that do not overlap with each other, and need additional energy of phonons. In fact, the key role played by the hosting phonon is to fill the energy gap to allow energy transfer. This mechanism occurring among donor-acceptor is interesting since it allows to maximize mutual information in our model by varying the dopant concentration.

In a donor-acceptor scenario, normally the energy transfer probability (*i.e.*, P_{ET}) is regulated by the Förster-Dexter theory and this probability is proportional to the spectral overlap integral of the donor's emission and acceptor's absorption. For

[1]Let us recall that the relation between 1 Joule and wavenumber cm^{-1} is as follows: $1 Joule(J) = 5.034 \times 10^{22} cm^{-1}$.

certain systems, the overlap integral is poor and the host lattice vibrational energy, normally a phonon, plays the key role as bridging the difference of the energy (*i.e.*, ε as in Fig. 4). The energy transfer probability will be computed as [1]:

$$P_{ET} \propto I(E_{ph}) = \frac{e^{E_{ph}/K_{BT}}}{e^{E_{ph}/K_{BT}} - 1} \int \frac{f_D(E - E_{ph}) f_A(E)}{E^2} dE, \tag{4}$$

where $f_D(E)$ is the line-shape function of donor's emission, $f_A(E)$ is the line-shape function of acceptor's absorption and E_{ph} is the host phonon energy. $I(E_{ph})$ is defined as the phonon-assisted overlap. In this work, we focus on the role of phonon to match the energy gap for an efficient $Nd^{3+} \rightarrow Yb^{3+}$ transfer constituting the information transfer in two different dopant glasses.

Equation (4) is a generalization of the Dexter model, such as:

$$W_t \propto \int \frac{f_D(E) f_A(E)}{E^2} dE, \tag{5}$$

where W_t is the energy transfer probability based on the Dexter model [34]. The relation (4) gives us an estimation of non-resonant energy transfer processes (as $Nd^{3+} \rightarrow Yb^{3+}$) in particular host material.

Another measure for the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer which is more quantifiable is the energy transfer efficiency η_{ET}. In particular, the energy efficiency η_{ET} can be calculated based on spectral data through Eq. (6) [32], [35], where $\eta_{Nd}(\approx 0.76)$ and $\eta_{Yb}(\approx 0.95)$ are quantum yields of Nd^{3+} and Yb^{3+} ions respectively. β is the branching ratio, $I(t)$ represents the emission intensity.

An alternative way to compute the energy transfer efficiency is based on the luminescence decay of the donor (*i.e.*, Nd^{3+} in this context) in co-doped samples as [1]:

$$\eta_{ET} = 1 - \frac{\tau_{Nd-Yb}}{\tau_{Nd}}, \tag{7}$$

where τ_{Nd} and τ_{Nd-Yb} represent the Nd^{3+} fluorescence decay time for single and co-doped samples, respectively.

In this work, we focus on the impact of the dopant concentrations on the channel model, specifically in terms of channel capacity as maximization of mutual information. Indeed, the rules governing the energy transfer (*i.e.*, the data information transfer) are based on different models that exploit donor and acceptor concentrations. As explained in [2] and [36], as the donor concentration (in this specific case, the concentration of Nd^{3+}) is low, the information transfer follows the direct donor to acceptor path. In this kind of context it is extremely important to define two microparameters related to the energy transfer that occur between donor and acceptor, and among donors. In particular, we define C_{DA} as the microscopic energy transfer parameter between donor and acceptor, and C_{DD} as the donor-donor energy migration parameter. If the $C_{DA} > C_{DD}$ (*i.e.*, low donor concentration), the energy transfer is governed by static and direct donor-to-acceptor mechanisms. As the donor concentration increases, there are donor-donor interactions that have to be considered, and usually the energy/information migration occurs through hopping mechanisms. In this specific case, the Burshtein model is applied for decay analysis and the luminescence decay intensity *i.e.*, $I(t)$, is calculated as [1]:

$$I(t) = I_0 \exp\left[-\frac{t}{\tau_0} - \frac{4\pi}{3} N_A \Gamma\left(1 - \frac{3}{s}\right)(C_{DA} t)^{3/s} - W_m t\right], \tag{8}$$

where N_A represents the acceptor ion concentration, Γ is Euler's gamma function, and s is electrostatic interaction parameter *i.e.*, $s = 6$ for dipole-dipole interactions, and $W_m t$ is the migration parameter.

The microscopic energy transfer parameters C_{DA} and C_{DD} depend on the specific characteristics of the host material and can be calculated as [1]:

$$C_{DX} = \frac{3c}{8\pi^4 n^2} \int \sigma_{em}^{D}(\lambda) \int \sigma_{abs}^{X}(\lambda) d\lambda, \tag{9}$$

where $X = \{A, D\}$, c is the light velocity in vacuum, n is the refractive index, and $\sigma_{em}^{D}(\lambda)$ and $\sigma_{abs}^{X}(\lambda)$ are the emission and absorption cross-sections donor and acceptor/donor, respectively. Of course, in the specific case we are considering, the computation of energy transfer micro-parameters has to include the energy transfer components. This is done by considering the Stoke's phonon sidebands to the absorption and emission cross section spectra based on the Auzel law [23], *i.e.*:

$$\sigma_{Stokes} = \sigma_{elect} \exp(-\alpha_s \Delta E), \tag{10}$$

where α_s represents the host dependent parameter for Stoke's transitions, and ΔE represents the mismatch between electronic and vibrational transitions. In particular α_s is depending on a parameter $\overline{N}$ that represents the number of phonons necessary for compensate the energy gap. More specifically, α_s is calculated as:

$$\alpha_s = (h\nu_{\max})^{-1} \left(\ln\left\{\left(\overline{N}/S_0\right)\left[1 - \exp\left(h\nu_{\max}/kT\right)\right]\right\} - 1\right), \tag{11}$$

where S_0 is the electron-phonon coupling constant (≈ 0.04), $h\nu_{\max}$ is the maximum phonon energy of host, k is the Boltzmann constant and T is the temperature.

In this work, we focus on the estimation of the channel capacity in specific glasses by varying the dopant concentration with two different matrix hosts, and then we have to take into consideration the energy transfer micro-parameters as computed above. The first scenario concerns $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer in alkali-free barium-alumino-metaphosphate glasses, while the second scenario regards the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer in a series of heavy metal oxide based zinc-boro-bismuthate glasses. Both the series are characterized by the fact that the energy transfer is not resonant, but is phonon-assisted.

IV. Channel Capacity Derivation

The upconversion phenomenon can be revisited from an information theory point of view, as a communication channel between a transmitter nanomachine (TN) and a receiver nanomachine (RN), where the bit stream is modulated through an OOK scheme. Specifically, as depicted in Fig. 5, we model the communication channel as a Z-channel, where the variable

$$\eta_{ET} = \frac{\eta_{Yb}^{-1} \int_{850nm}^{1100nm} I_{Em}^{Yb}(\lambda) d\lambda}{\eta_{Nd}^{-1} \left(1 + \frac{\beta_{4_{I_{13/2}}} + \beta_{4_{I_{15/2}}}}{\beta_{4_{I_{9/2}}} + \beta_{4_{I_{11/2}}}}\right) \int_{850nm}^{1100nm} I_{Em}^{Nd}(\lambda) d\lambda + \eta_{Yb}^{-1} \int_{850nm}^{1100nm} I_{Em}^{Yb}(\lambda) d\lambda}, \tag{6}$$

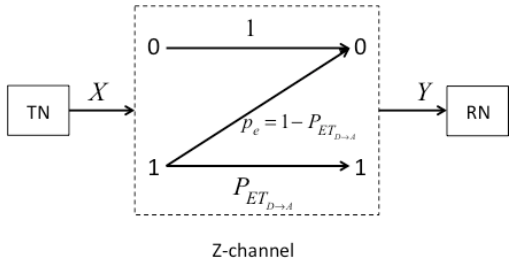

Fig. 5. PAET channel model as a Z-channel.

X represents the bit 1 or 0 transmitted along the channel, while Y is the received bit (*i.e.*, 1 or 0), based on a probabilistic approach. Indeed, the presence of a bit 1 at the receiver means that a bit 1 has been transmitted with conditional probability $\Pr(Y = 1|X = 1)$, while a bit 0 at the receiver side can be affected by errors in the channel corresponding to the error probability $p_e = \Pr(Y = 0|X = 1)$, in case of a bit 1 transmitted with errors. Notice that, differently from traditional OOK-based communication schemes for molecular communications, in this paper the OOK modulation is not based on the concentration variation of the molecules, but on the energy transfer between a couple donor-acceptor. In practice, a bit 1 is associated to the energy transfer occurrence, while a bit 0 is associated to no excitation of the donor.

The Z-channel shown in Fig. 5 has been revised in the context of upconversion phonon-assisted mechanism. We assume a time-based synchronization scheme at the transmitter side, then the transmission of a bit 1 corresponds to a laser that excites donors at the beginning of a time slot, while no excitation corresponds to the emission of a bit 0. P_{NE} corresponds to the probability to send a bit 0 in the case of no excitation at the beginning of the time slot. If no excitation is provided to the TN, then no energy transfer will occur (*i.e.*, from the information theory point of view, no transmission errors will occur, while transmitting bit 0).

The probability that the bit 1 is correctly received by the receiver corresponds to the probability of energy transfer from donor to acceptor, namely $P_{ET_{D\to A}}$. This probability can be considered to be equal to the energy transfer efficiency η_{ET} and can be calculated using (7) or (6). The failure probability of transmitting a bit 1 when the donor is excited is $(1 - P_{ET_{D\to A}})$.

Notice that a similar model has been proposed for the FRET approach in [33]. The main difference between our proposed approach and the technique in [33] is that we consider a PAET system, where not only it is important to evaluate the impact of phonon energy variation from an information theory point of view, but also the impact of dopant concentrations. In the case of FRET, there is the constraint in terms of spectrum overlapping of the donor and acceptor, which is poor in the context considered.

For the moment, we disregard external noise factors such as self-quenching phenomenon, multi-phonon relaxation effect or acceptor-to-donor energy back transfer. In particular, self-quenching mechanism can be evaluated by computing the micro-parameter C_{DA}^{Nd-Nd}, which has to be kept as low as possible in order to maximize the energy transfer between donor and acceptor. In fact, $C_{DA}^{N_d-N_d}$ is a loss term and high values signify depopulation of the ions that allow the energy transfer through a cross-relaxation mechanism before actual transfer to Yb^{3+} ions.

Although we disregard the external noise factors, the channel acts like a noisy channel since the probability of energy transfer occurrence is intrinsically not equal to 1 *i.e.*, $P_{ET_{D\to A}} \neq 1$. According to the transmission probabilities, the transition matrix of the Z-channel considering X as the transmitted bit by the TN, and Y as the received bit by RN is given as

$$\begin{aligned} &\Pr(Y|X) = \\ &= \begin{bmatrix} P_{NE} & 0 \\ (1 - P_{ET_{D\to A}}) & P_{ET_{D\to A}} \end{bmatrix}, \end{aligned} \tag{12}$$

where P_{NE} corresponds to the a priori probability of sending bit 0 which corresponds to no excitation by NIR source and is equal to 1.

From (12), we can easily derive the mutual information between X and Y as follows:

$$\begin{aligned} I(X;Y) = &H\left(P_{ET_{D\to A}}(1 - P_{NE})\right) \\ &- (1 - P_{NE}) H\left(1 - P_{ET_{D\to A}}\right), \end{aligned} \tag{13}$$

where $H(\cdot)$ represents the binary entropy. As known, from (13) we can compute the channel capacity for the PAET system (*i.e.*, C_{PAET}) as the maximum of mutual information *i.e.*,

$$\begin{aligned} &C_{PAET} = \\ &\max_{P_{NE}} \left[H\left(P_{ET_{D\to A}}(1 - P_{NE})\right) - (1 - P_{NE}) H\left(1 - P_{ET_{D\to A}}\right)\right]. \end{aligned} \tag{14}$$

The probability distribution of input, *i.e.*, P_{NE} that maximizes the capacity will change according to specific dopant concentrations for different glasses considered.

V. Numerical Results

In our analysis, we aim to investigate the channel capacity for different conditions such as varying donor and acceptor concentration in host glass and phonon energy corresponding to host glass in order to determine the optimum conditions allowing the highest capacity. It is worth to recall that in our PAET-based communication system the donor acts as transmitter and the acceptor as a receiver. Of course, different concentrations of donors and acceptors may impact on the energy and information transfer efficiency.

In this section, we consider four different scenarios for the energy transfer of the couple Neodymium and Ytterbium ions (*i.e.*, $Nd^{3+} \rightarrow Yb^{3+}$) where we vary energy transfer efficiency estimation method (*Scenario 1*), donor concentration (*Scenario 2*), acceptor concentration (*Scenario 3*), and phonon energy (*Scenario 4*) for three different host materials. The three host materials are three different glasses doped with Nd^{3+} and Yb^{3+} ions, namely, (*i*) yttrium aluminum tetraborate glasses (*i.e.*, $YAI_3(BO_3)_4$) (*Host 1*), (*ii*) alkali-free barium-alumino-metaphosphate glasses (*i.e.*, Alkali-free $BaAlPO^{3^-}$) (*Host 2*), and (*iii*) co-doped zinc-boro-bismuthate glasses (*i.e.*, co-doped $ZnBBiO^{3-}$) (*Host 3*). These four scenarios are explained in details in the following sections and each scenario is studied from an information theory point of view, by computing the channel capacity from (13).

Finally, we will derive the error probability for our PAET system, as well as information about energy delay occurring in the PAET-based channel model.

A. Energy Transfer Efficiency Estimation

In this section we consider *Scenario 1* where we compare two different energy transfer efficiency estimation methods. Energy transfer efficiency can be calculated either from fluorescence spectra (FS) using Eq. (6) or from fluorescence decay (FD) profile using Eq. (7). To compare the capacities computed using these two methods we consider the zinc-boro-bismuthate ($ZnBBiO^{3-}$) glass co-doped with Nd^{3+} and Yb^{3+} ions (*Host 3*). In this first scenario, the energy transfer efficiency is obtained for different concentration of acceptor (Yb^{3+}) in this glass. $N05YXX$ corresponds to $XX/10\ mol\%$ of Yb^{3+} in the glass.

The experimental values of energy transfer efficiency for these two methods are given in Table I. According to these values, the capacity of this PAET channel is plotted in Fig. 6. At low acceptor concentration, the two methods are in close agreement, however as the concentration of Yb^{3+} increases the discrepancy between the two curves increases. This is due to the intermixing of Nd^{3+} emission with the tail of end of Yb^{3+} emission [2]. Based on the different types of glasses considered as host material, the doped glass has different properties. In the specific case, the emission spectrum of Nd^{3+} is slightly red, shifted towards 900 nm and then there is an intermixing between the emission of Nd^{3+} with the activity of Yb^{3+}. For these reasons, this type of efficiency, based on time decay, cannot be considered trustable to characterize the energy transfer. This effect causes a wrong estimation of fluorescence decay profile and energy transfer efficiencies calculated from FD. Hence, we will use the energy transfer efficiencies computed from the fluorescence spectra (FS) of donor and acceptor for the rest of the paper.

Another important observation from Fig. 6 is the saturation of capacity for high acceptor, *i.e.*, Yb^{3+}, concentrations arising from the fixed donor concentration limiting the energy transfer. Since there is not enough donor, increasing acceptor concentration does not increase capacity indefinitely.

TABLE I
EXPERIMENTAL VALUES OF ENERGY TRANSFER EFFICIENCY USED IN SCENARIO 1, FOR DIFFERENT DOPANT CONCENTRATIONS AND APPROACHES [2].

Glass	Energy Transfer Efficiency (%)	
	Fluorescence decay	Fluorescence spectra
N05Y01	10.7	16.4
N05Y05	34.5	69.8
N05Y10	44.3	87.7
N05Y15	49.1	87.1

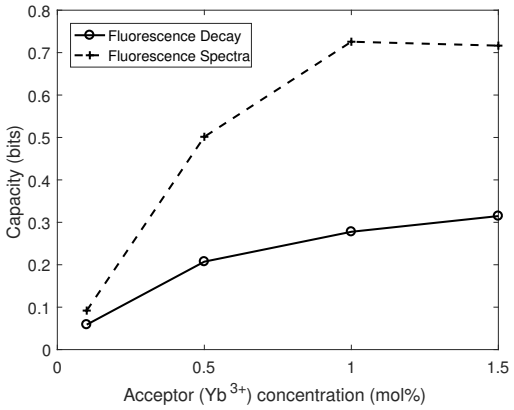

Fig. 6. Capacity (bits) vs. donor (Nd^{3+}) concentration to compare energy transfer estimated using fluorescence decay (FD) time and sensitized fluorescence spectra (FS). Experimental results are taken from [2].

1) Impact of Donor Concentration on Channel Capacity: *Scenario 2* corresponds to investigating the impact of donor, *i.e.*, Nd^{3+}, concentration on the capacity of PAET channel. For this scenario we consider $YAI_3(BO_3)_4$ glass as the host material (*Host 1*). We use the energy transfer efficiency values from Table II corresponding to different donor (Nd^{3+}) concentrations [35].

The mutual information is plotted against P_{NE}, the probability of sending bit 0 in Fig. 7 for different concentrations of Nd^{3+}. It is observed that the maximum of mutual information is attained for $P_{NE} = 0.6$. Hence, to achieve the maximum mutual information we should send more 0's than 1's. Furthermore, in Fig. 8, it is clearly seen that as donor concentration increases the mutual information also increases as expected. Therefore, to achieve a higher capacity, we can use a glass which is more heavily doped with the donor ion. For the most heavily doped glass the capacity reaches $C_{PAET}^{S_2} = 0.4241$ bits.

2) Impact of Acceptor Concentration on Channel Capacity: In this section, we study the effect of acceptor concentration in the host glass as *Scenario 3*. Specifically, we consider the couple Neodymium and Ytterbium ions for the energy transfer (*i.e.*, $Nd^{3+} \rightarrow Yb^{3+}$) in (*i*) alkali-free barium-alumino-metaphosphate glasses (*i.e.*, Alkali-free $BaAlPO_3^-$) (*Host 2*).

This type of analysis can give us important information to evaluate the effectiveness of varying the concentration of acceptor in order to maximize the mutual information, and then to derive the channel capacity.

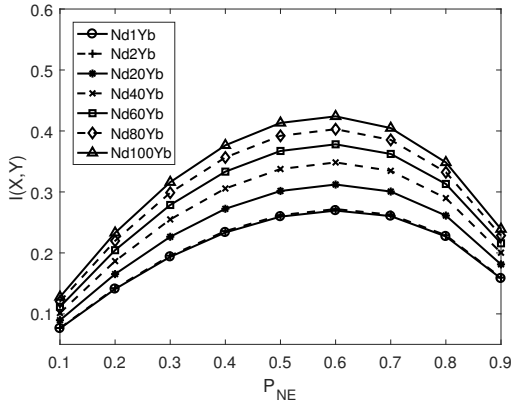

Fig. 7. Mutual information (bits) vs. P_{NE} for various donor (Nd^{3+}) concentrations. $NdXYb$ represents each host glass with X % mol Nd^{3+} concentration. Experimental results are taken from [35].

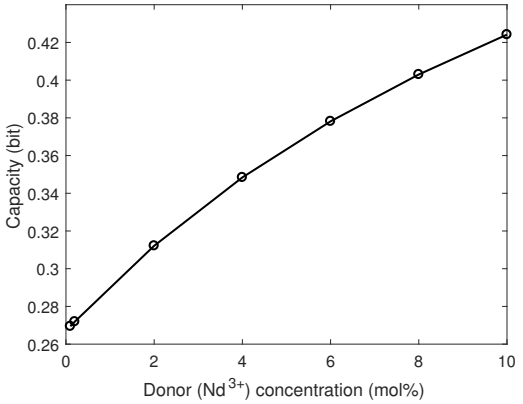

Fig. 8. Capacity (bits) vs. donor (Nd^{3+}) concentration. Experimental results are taken from [35].

In scenario S_2, the mutual information with respect to P_{NE} for glasses with different acceptor, *i.e.*, Yb^{3+}, concentrations is illustrated in Fig. 9. It is observed that the mutual information increases with increasing acceptor concentration. Furthermore, the value of P_{NE} bearing the maximum capacity shifts from 0.61 for $Yb005$ to 0.49 for $Yb090$. We can conclude that the probability of sending 0's, *i.e.*, P_{NE}, should be adjusted according to the acceptor concentration in the glass to maximize the capacity.

The channel capacity for this scenario is plotted against the acceptor concentration is Fig. 10. The channel capacity sharply increases for increasing acceptor concentration at low acceptor concentration. However, after a point this increase slows down and saturates since there is limited donor atoms in the glass.

The value of channel capacity for maximum acceptor concentration is $C_{PAET}^{S_3} = 0.867$ bit. Experimental values used in this simulation are collected in Table II for Scenario 3.

3) Impact of Phonon Energy Level on Channel Capacity: Another factor affecting the energy transfer in PAET is the variation of phonon energy (*i.e.*, E_{ph}). Here, we again consider the case of $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer in co-doped Ba-Al-metaphosphate glasses (*i.e.*, co-doped $BaAlPO_3^-$) (*Host 2*). In this scenario 4 ($S4$), we investigate the channel capacity for different phonon energy levels. Experimental values of phonon energy corresponding to single-doped glasses in Ba-Al-metaphosphate are taken from [1].

TABLE II
EXPERIMENTAL VALUES OF ENERGY TRANSFER EFFICIENCY USED IN SCENARIO 2 AND 3

Scenario 2, for different donor concentration [35]	
Glass	**Energy Transfer Efficiency** (%)
Nd1Yb	43.2
Nd2Yb	43.53
Nd20Yb	48.77
Nd40Yb	53.25
Nd60Yb	56.76
Nd80Yb	59.58
Nd100Yb	61.9
Scenario 3, for different acceptor concentration [1]	
Glass	**Energy Transfer Efficiency** (%)
BAP-NdYb005	10.7
BAP-NdYb01	16.0
BAP-NdYb05	47.9
BAP-NdYb10	64.2
BAP-NdYb30	86.5
BAP-NdYb60	93.2
BAP-NdYb90	95.1

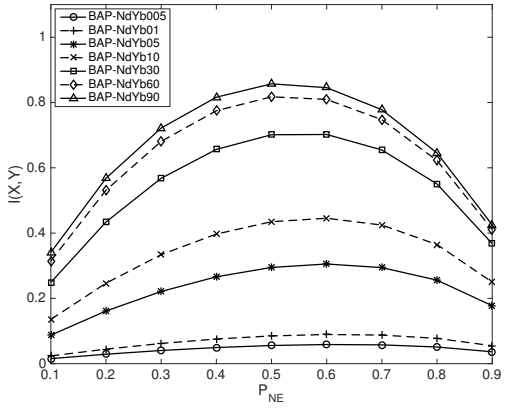

Fig. 9. Mutual Information vs. P_{NE} for various values of acceptor concentration. Experimental results are taken from [1].

The energy transfer probability values give an idea of the phonons required in order the energy transfer to occur with a certain efficiency. The energy transfer probability increases with the increase of energy phonon. The maximum is attained in the range $[900, 1200]$ cm^{-1}.

In Fig. 11, channel capacity versus phonon energy level is plotted. It is interesting to observe in Fig. 11 that the maximum of mutual information is obtained for a range of phonon energy levels $[900-1200]$ cm^{-1} matching the type of phonons needed in order the energy transfer process to occur.

In this case, the value of channel capacity is $C_{PAET}^{S_4} = 0.872$ bit. Comparing the proposed PAET-based model to the FRET-based channel model [33], we observe the highest capacity is 0.864 bit, which is achieved for a FRET probability corresponding to 0.5.

The values for channel capacity for PAET obtained in this

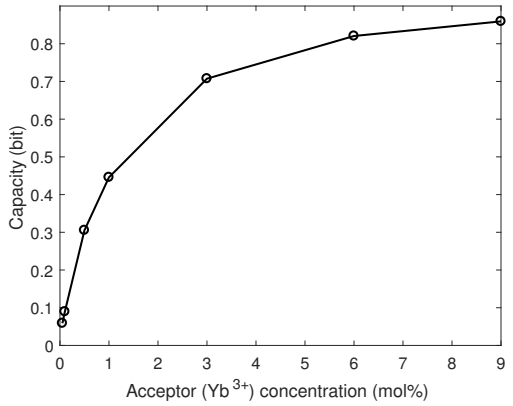

Fig. 10. Capacity (bits) vs. acceptor (Yb^{3+}) concentration. Experimental results are taken from [1].

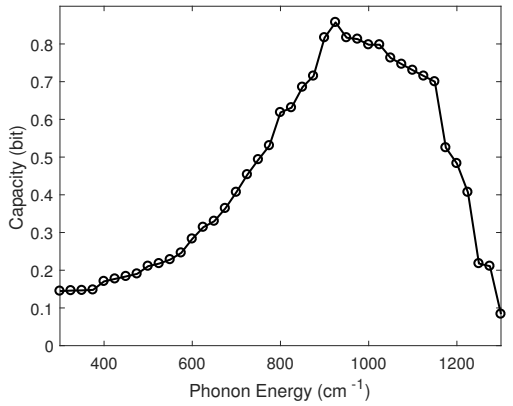

Fig. 11. Mutual information [bit] vs phonon energy in scenario S_4. Experimental results are taken from [1].

paper are slightly higher compared to capacities of FRET [33]. However, by adjusting the donor, acceptor concentration and choosing the right host material, these capacities can be pushed further. The advantage of PAET over FRET is that the energy levels of donor and acceptor atoms do not need to be exactly matching. By the assistance of phonons closing the energy gap, the energy transfer occurs more frequently, hence PAET channel can transfer more information compared to FRET channels.

B. Error Probability Derivation

In this section we describe a noise model associated to the channel model above described. The theoretical derivation is general and can be applied to all the PAET systems, while numerical results refer to the zinc-boro-bismuthate glasses.

There are several sources of noise, such as non-radiative energy losses of donor ions due to multiphonon relaxation resulting in lower quantum yield, self-quenching, and energy back transfer. In this work, we will derive a BER analysis based only on self-quenching, since in the type of scenario considered it can cause significant loss of excitation energy compared to the multiphonon relaxation phenomenon. The acceptor-donor energy back-transfer could impact a lot on the efficiency of the system when it occurs. In the two scenarios considered in this work, *i.e.* (*i*) the barium-alumino-metaphosphate and (*ii*) zinc-boro-bismuthate glasses, the excitation spectrum of acceptor-donor was considered in order to verify if there was evidence of $Nd^{3+} \leftarrow Yb^{3+}$ energy back transfer. It has been concluded that it is three order of magnitude smaller than the direct energy transfer (*i.e.* $Nd^{3+} \rightarrow Yb^{3+}$) in the ba-al-metaphosphate, and it is absent in the zn-bo-bismuthate case. Due to these reasons, we have neglected the inclusion of the energy back transfer in the noise model.

It is well-known that the distribution of the output signal for an OOK system at the receiver is [37]:

$$p_1(r) = \frac{r}{\sigma^2} \exp\left(-\frac{r^2 + A^2}{2\sigma^2}\right) I_0\left(\frac{Ar}{\sigma^2}\right), \tag{15}$$

and

$$p_0(r) = \frac{r}{\sigma^2} \exp\left(-\frac{r^2}{2\sigma^2}\right), \tag{16}$$

where p_1 represents the probability distribution when a bit 1 is sent, r is the received signal, I_0 is the zero-order modified Bessel function of the first kind and p_0 represents the probability distribution associated to the transmission of a bit 0.

Let us define $P_e^{1,0}$ as the error probability of a bit 1 being received as a bit 0, and $P_e^{0,1}$ as the error probability of a bit 0 being received as a bit 1, defined respectively as follows:

$$P_e^{1,0} = \exp\left(-\frac{b^2}{2\sigma^2}\right), \tag{17}$$

and

$$P_e^{0,1} = 1 - Q\left(\sqrt{2\frac{E_b}{N_0}}, \frac{b}{\sigma}\right), \tag{18}$$

where Q is a Marcum-Q function, σ^2 is the standard deviation of the noise, and b represents a decision threshold that in our case coincides with the amount of energy needed to fill in the metastable state gap, and allows the light emission. More specifically, b is defined as:

$$b = \sigma\sqrt{2 + \frac{E_b}{2N_0}}. \tag{19}$$

Theoretically, from (17) and (18) the BER is as:

$$P_e = \frac{1}{2}\left[1 - Q\left(\sqrt{2\frac{E_b}{N_0}}, \frac{b}{\sigma}\right) + \exp\left(-\frac{b^2}{2\sigma^2}\right)\right]. \tag{20}$$

In the specific scenario we are considering, the probability that a bit 0 is sent and is detected as a bit 1 can be neglected, since a bit equal to 0 corresponds to the absence of source power, and for the moment we neglect the fact that there could be an energy transfer even in absence of a specific source power.

The error probability in (20) is then represented by the contribution of $P_e^{1,0}$ only. After some calculations, (20) becomes:

$$P_e = \frac{1}{2}\left[\exp\left(-\frac{1}{2}\left(2 + \frac{E_b}{2N_0}\right)\right)\right]. \tag{21}$$

In the specific context we are considering the estimation of E_b and N_0 have to be related to micro-parameters of the system, named C_{DA}^{Nd-Yb} and C_{DA}^{Nd-Nd}, which represent the energy transfer micro-parameters. C_{DA}^{Nd-Yb} characterizes the energy transfer activity between the donor and the acceptor. Higher values of this parameter are significant of an efficient energy/communication transfer. The micro-parameter C_{DA}^{Nd-Nd} represents an undesired self-quenching effect, that is an energy/communication transfer between donor-donor. These micro-parameters [1], [2] are calculated on the basis of the emission and absorption spectra of a donor and an acceptor. C_{DA}^{Nd-Yb} has been found equal to $3.47 \times 10^{-39} cm^6 s^{-1}$ in zinc-boro-bismuthate glasses, corresponding to $1.65 \times 10^{-39} cm^6 s^{-1}$ in barium-alumino-metaphosphate glasses. On the other hand, the value of C_{DA}^{Nd-Nd} has been estimated equal to $0.018 \times 10^{-39} cm^6 s^{-1}$ for zinc-boro-bismuthate *i.e.*, a low value that allows keeping low the undesired self-quenching effect, and it has been found equal to $0.004 \times 10^{-39} cm^6 s^{-1}$ in the case of barium-alumino-metaphosphate glasses.

The theoretical energy transfer between donor and acceptor is related to the acceptor concentration and can be derived as

$$\gamma_{DA(Nd-Yb)}^2 = \frac{16\pi^3}{9} C_{DA}^{(Nd-Yb)} N_A^2, \tag{22}$$

while the self-quenching effect that is also depending on the donor concentration is

$$\gamma_{DA(Nd-Nd)}^2 = \frac{16\pi^3}{9} C_{DA}^{(Nd-Nd)} N_D^2. \tag{23}$$

In our system, $\gamma_{DA(Nd-Yb)}^2$ represents the part of "desired" signal as E_b, while $\gamma_{DA(Nd-Nd)}^2$ represents the "undesired" component N_0, that is noise. Based on such a consideration, it follows that:

$$\frac{E_b}{N_0} \approx \frac{\gamma_{DA(Nd-Yb)}^2}{\gamma_{DA(Nd-Nd)}^2}. \tag{24}$$

This result is in accordance with the dependence of the system performance to the concentration of the dopant (both donor and acceptor concentrations). In Fig. 12 we depict the error probability versus the donor concentration in case of (*i*) zinc-boro-bismuthate and (*ii*) barium-alumino-metaphosphate glass. We can observe how the higher is the donor concentration the higher is the impact of self-quenching on the system (from left to right in the figure) with an higher error probability (*i.e.*, corresponding to a missing delivery of the bit 1 at the receiver). The concentration of acceptor has been kept constantly equal to $0.1 mol\%$ for the two scenarios.

In Fig. 13 we consider a donor concentration of $10 mol\%$ and we vary the acceptor concentration. We can observe that the increasing of acceptor concentration has a positive impact in terms of error probability, since the self-quenching effect due to the donor concentration is mitigated by the presence of more acceptors. This result validates the reasoning about the main impact played by the dopant (*i.e.*, acceptor and donor) concentration on the performance of the system. Moreover, in Fig. 10 we have shown that the acceptor concentration plays a key role on the communication capacity of the channel, confirmed by the small values of the error probability in Fig. 13.

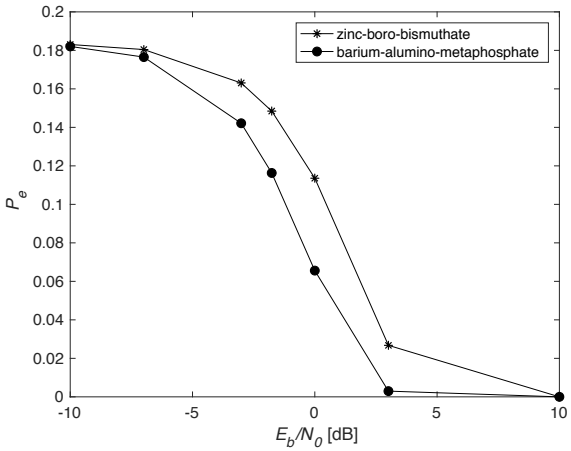

Fig. 12. Impact of self-quencing on the error probability vs. the donor concentration (expressed in terms of E_b/N_0) in the zinc-boro-bismuthate glass and barium-alumino-metaphosphate glass. Acceptor concentration is equal to $0.1 mol\%$. An higher donor concentration increases the error due to an self-quenching effect. Experimental data are taken from [1], [2].

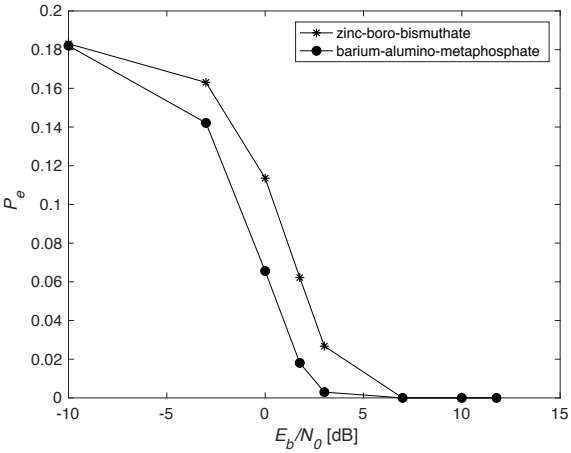

Fig. 13. Error probability vs. the acceptor concentration (expressed in terms of E_b/N_0) in the zinc-boro-bismuthate glass and barium-alumino-metaphosphate glass. Donor concentration is equal to $10 mol\%$. An higher acceptor concentration allows to emphasize the direct energy/information transfer effect in respect of the self-quenching phenomenon. Experimental data are taken from [1], [2].

C. Delay Considerations

In this section we make some considerations about the speed of the energy/information transfer process when the acceptor concentration varies. More specifically, we make reference to the time needed to transfer a bit 1 from a donor/transmitter to an acceptor/receiver. Again, we make reference to barium-alumino-metaphosphate glasses scenario and we consider a constant donor concentration of $1 mol\%$, while concentrations of donor are varied as $[0.005, 0.01, 0.05, 10, 30, 60, 90]$ $mol\%$. The delay is derived by considering the energy transfer rate for all the samples. In Fig. 14 we can observe that the PAET transfer mechanism is faster when acceptor concentration is higher. Worst result (*i.e.*, ≈ 2.5 ms) is for very low acceptor concentration.

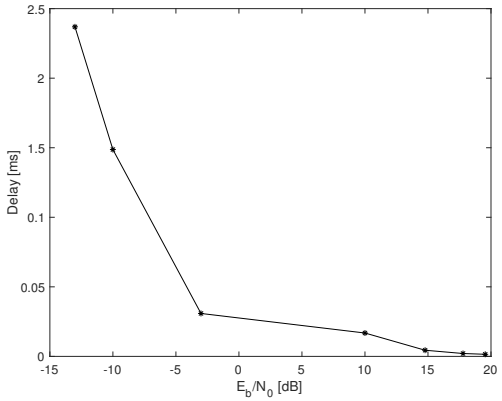

Fig. 14. Estimated time required for energy/information transfer in barium-alumino-metaphosphate glasses with constant donor concentration equal to $1mol\%$, vs. the acceptor concentration (expressed in terms of E_b/N_0). Experimental data are taken from [1].

VI. Conclusions and Future Perspectives

In this paper, we have investigated on upconversion phenomenon as enabler for molecular optical channel modeling. Upconversion process is gaining a lot of interest from scientific and research community above all in medical applications domains. It is mainly related with rare-earth components as upconversion nanoparticles, and it has been shown that these components have very interesting features for *in-vivo* applications, such as high values of signal-to-noise ratio, the capability to "convert" NIR radiation into visible light spectrum allowing a deeper signal penetration in the tissue in a safely way, low cyto-toxicity level, etc. These specific features are interesting from a communication point of view and represent the leitmotif of our research in molecular optical communications.

In this paper we have derived an initial information theory analysis on a one-to-one communication scheme with a pair of donor-acceptor playing the role of transmitter and receiver, respectively. As a first approach, and as the main objective to show the feasibility of our approach, we have associated to the communication system an On-Off-Key modulation scheme by deriving the theoretical capacity of the global system, by varying the dopant (nanoparticle nodes) concentration. Moreover, we have derived a theoretical and general analysis of noise sources for PAET communication systems, which have been applied to the specific scenario of zinc-boro-bismuthate material thanks to experimental results published in literature. This analysis has validated the key role played by the dopant/nanoparticles concentrations in similar systems.

The research area around processes as FRET, PAET, etc. as enablers for communications at molecular level is at its beginning. However, a deep analysis of this type of phenomena could pave the way of communication at a nano-size. In-depth knowledge of the mechanisms underlying these processes could allow the birth of new types of research in the context of metamaterials, and also software defined metamaterials, where the features (*e.g.* orientation, shape. etc.) of portions of a material could be modified in order to boost a certain type of reactivity or process.

In this work, we have highlighted as optical properties of specific matter, such as RE-doped materials, are suitable to improve energy transfer efficiency and consequently the information transfer. A major control of these optical properties could allow the design of specific mechanisms to "store" the signal as in traditional communication systems with buffer. Finally, another important perspective is concerning the possibility to use different types of colors in the emitting signals. This aspect could be efficiently exploited to design specific color-based modulation schemes such as Color-Shift-Keying (CSK), to improve the total communication capacity of the system.

As a lesson learned, we state that phonons could play a fundamental role in upconversion-based communication systems, and deeper analysis related to these quantum particles will be of great importance to advance in this research field. When investigating this type of mechanism as enabler for molecular optical communication systems, a deeper understanding of the inherent processes allows better control on specific components of the mechanisms. In other words, we have realized that just by changing the concentration of donor/acceptor ions in a host material, we can tune the channel capacity of an upconversion communication system. Finally, a multi-hop PAET system can be created by taking advantage of energy migration upconversion (EMU), where the acceptor atom transfers the energy received from the donor to another acceptor atom. Using EMU in core-shell nanoparticles, the information can be transferred over multi-hop to longer distances.

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